

## PATENT SPECIFICATION

(11) 1359 023

33 (21) Application No. 51714/71 (22) Filed 8 Nov. 1971  
 32 (21) Application No. 51715/71 (22) Filed 8 Nov. 1971  
 0 (23) Complete Specification filed 23 Oct. 1972  
 2 (44) Complete Specification published 3 July 1974  
 16 (51) International Classification C07C 17/00  
 10 (52) Index at acceptance

C2C 200 20Y 304 311 313 31X 31Y 339 410 413 414  
 416 440 441 442 443 444 445 44X 564 565 566  
 567 65Y 73Y HA HJ

(72) Inventors DAVID HENRY COOPER and  
 DONALD LOMAS



## (54) MANUFACTURE OF PERCHLOROFLUOROMETHANES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the manufacture of perchlorofluoromethanes.

It is known that aliphatic and partially-chlorinated aliphatic hydrocarbons can be brought into reaction with hydrogen fluoride and chlorine in the absence of a catalyst at a temperature of from 300°C to 500°C to give fluorinated alkanes. However such a chlorohydrofluorination reaction is not completely satisfactory in that there is an undesirably wide spectrum of fluorinated alkanes in the reaction product and/or that yields of chlorofluoromethane are low, particularly of chlorofluoromethanes containing two fluorine atoms in the molecule. The teachings has been that excessive reaction temperatures can cause pyrolysis and carbonisation and accordingly it has been disclosed that the reaction must not be carried out at a temperature exceeding 500°C. Indeed temperatures of from 350°C to 450°C have been preferred for the reaction.

We have now surprisingly found that eminently useful results can be obtained in the chlorohydrofluorination of certain aliphatic hydrocarbons and halogenated aliphatic hydrocarbons at temperatures in the range 525°C to 700°C.

According to the present invention we provide a process for the manufacture of a perchlorofluoromethane which comprises bringing into reaction an aliphatic hydrocarbon having three carbon atoms or a halogenated aliphatic hydrocarbon (as hereinafter defined having one to three carbon atoms with hydrogen fluoride and chlorine in the absence of a

particulate catalyst at a temperature in the range 525°C to 700°C.

The term "catalyst" as used herein includes elemental carbon.

By the term "a halogenated hydrocarbon" as used throughout the present specification is meant an aliphatic hydrocarbon in which all or some of the hydrogen atoms in the hydrocarbon have been replaced by chlorine or fluorine or a combination thereof, other than a fully-fluorinated hydrocarbon.

Preferably the reaction temperature is at least 550°C and temperatures in the range 575°C to 625°C are particularly preferred. It is a surprising feature of the present process that at the high temperatures employed and particularly with the preferred temperatures no pyrolysis or carbonation occurs while at the same time there is obtained a fully-halogenated reaction product which comprises mainly chlorofluoromethane having a significant proportion of dichlorodifluoromethane with respect to other halomethanes together with compounds which may be further reacted to give the aforesaid halomethanes.

Mixtures of the hydrocarbons and/or the halogenated hydrocarbons may be used if desired. The hydrocarbons and halogenated hydrocarbons may be saturated or unsaturated. Usually when a halogenated hydrocarbon is employed as organic starting material or as a component thereof it is preferred that it contains at least one hydrogen atom in the molecule. The present process may be utilised for the chlorohydrofluorination of chlorinated residues obtained in the production of chlorinated aliphatic hydrocarbons. Said residues may be obtained from oxychlorination processes, cracking processes and hydrochlorination processes which are utilised for instance in the manufacture of 1,2 - dichloroethylene, trichloroethylene, vinyl chloride and 1,1,1 - trichloroethane. Such residues often comprise mixtures predominating in partially chlorinated C<sub>2</sub> hydrocarbons which may be associated

50

55

60

65

70

75

80

85

90

with chlorinated C<sub>1</sub> hydrocarbons and a small amount of other chlorinated hydrocarbons such as chlorinated C<sub>2</sub> and C<sub>3</sub> hydrocarbons. Said residues may be fed with other organic starting materials to the reactor.

5 It is preferred to employ an organic starting material containing three carbon atoms in the molecule. Chlorinated C<sub>3</sub> hydrocarbons such as allyl chloride or propylene dichloride may be employed. Mixtures of such chlorinated hydrocarbons may be used. Good results are also obtained when using fluorinated C<sub>3</sub> hydrocarbons, for example, when using monofluoropropene, monofluoropropanes, difluoropropanes or mixtures of fluorinated C<sub>3</sub> hydrocarbons. These fluorinated hydrocarbons can conveniently be prepared by reaction of the appropriate unsaturated C<sub>3</sub> hydrocarbon with hydrogen fluoride at comparatively low temperatures of the order of 100°C to 120°C. Indeed in such a process a sufficient excess of hydrogen fluoride may be introduced with the unsaturated C<sub>3</sub> hydrocarbon to make the fluorinated material and to provide hydrogen fluoride for the chlorohydrofluorination reaction.

10 It is particularly preferred to employ a hydrocarbon containing three carbon atoms as organic starting material in the present process. Thus the C<sub>3</sub> hydrocarbon feed may comprise propane, propylene, methyl acetylene or allene. Again mixtures of C<sub>3</sub> hydrocarbons which are available commercially as a by-product of the petroleum industry and which have been of use only as a source of fuel are

15 eminently useful in the present process.

The proportion of hydrogen fluoride with respect to organic starting material may be varied over a wide range depending on the particular starting material, in particular on the number of carbon atoms and the degree of halogenation therein, and on the degree of fluorination required in the product. For example with a mixture predominating in a partially chlorinated C<sub>3</sub> hydrocarbon there may be employed 1.5 to 5 moles of hydrogen fluoride (and of chlorine) per mole of said partially chlorinated C<sub>3</sub> hydrocarbon. Again with a C<sub>3</sub> hydrocarbon, especially an unsaturated C<sub>3</sub> hydrocarbon or mixtures thereof, there

20 may be employed at least 3 moles and preferably at least 5 moles of hydrogen fluoride per mole of said unsaturated C<sub>3</sub> hydrocarbon. Up to 15 moles or more of hydrogen fluoride per mole of unsaturated C<sub>3</sub> hydrocarbon can be

25 employed. The proportion of chlorine with respect to organic starting material can also be varied over a wide range. Preferably at least 5 moles of chlorine and up to 12 moles chlorine per mole of unsaturated C<sub>3</sub> hydrocarbon are employed, although higher molar ratios of chlorine may be employed if desired.

30 In the present process there are obtained various by-products including chlorofluorocarbons containing two or three carbon atoms.

35 Worthwhile amounts of trichlorotrifluoroethane

(CFCl<sub>2</sub>. CF<sub>2</sub>Cl)

and dichlorotetrafluoroethane

(CF<sub>2</sub>Cl. CF<sub>2</sub>Cl)

may be obtained from the process. Most, or indeed all, of these by-products can be recycled to the process. The proportion of such recycled material to fresh organic feed is normally not high. Considerable proportions of perchloroethylene, for example 1 mole per mole of organic feed may be fed to the reactor or if preferred higher proportions may be recycled. Preferably reaction conditions are regulated so that the amounts of perchloroethylene entering and leaving the reactor are substantially constant.

40 The present process is eminently suitable for carrying out in a continuous manner and requires only a simple type of apparatus. Atmospheric or superatmospheric pressures, for example 2 to 20 atmospheres gauge can be employed. Superatmospheric pressures are useful in facilitating purification of the product. Contact times in the range 1 to 30 seconds, for example 1 to 10 seconds based on normal temperatures and pressures are suitably employed. The desired products can be recovered and purified using conventional means for example fractional distillation (or washing) techniques.

45 The following Examples illustrate the invention. In the Examples the apparatus consisted of a nickel tube 105 cms or 210 cms in length having an internal diameter of 2.5 cms. The tubes were heated over two-thirds of their length to the required temperature by means of external electrical heaters. The reactants were vaporised and preheated separately to temperatures up to 150°C before entering the reactor. The reactor off-gases were cooled, then passed through aqueous caustic solution to remove hydrogen chloride and any excess chlorine or hydrogen fluoride. The products were dried over calcium chloride. The volatile components of the reactor off-gases were liquified and analysed together with the non-volatile fractions using conventional techniques. No evidence of carbonation of the organic reactant was observed in any of the Examples.

#### Example 1

50 The reaction employed was 210 cm in length. Over a period of 3 hours and giving a contact time of 5.9 seconds a gaseous mixture of C<sub>3</sub> hydrocarbons (having the approximate composition propene 50%, propane 25%, a total of 25% methyl acetylene and allene) 20 parts, hydrogen fluoride 54 parts, and chlorine 345 parts was passed through the reactor maintained at 590°C. Analysis of the reactor off-gases (after removal of inorganic components) showed that the product com-

70

75

80

85

90

95

100

105

110

115

120

125

3

1,359,023

3

prised a mixture of perchlorofluorocarbons, composition of which is shown hereinafter.

		parts
5	1 CF <sub>2</sub> Cl <sub>2</sub>	11.6
	2 CFCI <sub>3</sub>	17.5
	3 CF <sub>3</sub> Cl	0.2
	4 CCl <sub>4</sub>	2.5
	5 C <sub>2</sub> Cl <sub>4</sub>	32.6
	6 C <sub>2</sub> Cl <sub>6</sub>	7.0
10	7 CF <sub>2</sub> ClCFCI <sub>3</sub>	0.4
	8 C <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub>	1.0
	9 CCl <sub>2</sub> FCCl <sub>3</sub>	2.3
	10 CFCI=CCl <sub>2</sub>	0.9

15 Compounds 4 to 10 inclusive were available for recycling. There was 100% conversion of the hydrocarbon mixture.

#### Example 2

The reactor employed was 105 cm in length. At a temperature of 600°C a gaseous mixture of C<sub>6</sub> hydrocarbons 20.9 parts, (the composition being as described in Example 1), together with chlorine 385 parts, and hydrocarbon fluoride 155 parts was passed through the reactor over a period of 3.5 hours giving a contact time of 4.0 seconds. After purification the analysis of the reactor off-gases showed that they were a mixture of perchlorofluorocarbons the composition of which was:—

		parts
30	1 CFCI <sub>3</sub>	29.2
	2 CF <sub>2</sub> Cl <sub>2</sub>	27.0
	3 CF <sub>3</sub> Cl	4.8
	4 CCl <sub>4</sub>	2.2
	5 CFCI <sub>2</sub> CFCI <sub>3</sub>	2.9
35	6 CFCI <sub>3</sub> CCl <sub>3</sub>	5.1
	7 CCl <sub>2</sub> CCl <sub>3</sub>	3.8
	8 CClF=CCl <sub>2</sub>	5.0
	9 CCl <sub>2</sub> =CCl <sub>2</sub>	24.9

40 Compounds 4 to 9 inclusive were available for recycling.

#### Example 3

The reactor used was 210 cm in length and was maintained at 613°C. There was passed through the reactor a gaseous mixture of C<sub>6</sub> hydrocarbon 17 parts (composition as described previously), chlorine 453 parts, hydrogen fluoride 56 parts and perchloroethylene 342 parts over a period of 3 hours. This gave a contact time of approximately 10 seconds. 50 The composition of the reactor off-gases after washing to remove inorganic materials was shown to be:—

		parts
55	1 CFCI <sub>3</sub>	101.3
	2 CF <sub>2</sub> Cl <sub>2</sub>	63.5
	3 CF <sub>3</sub> Cl	7.3
	4 CCl <sub>4</sub>	27.7
	5 C <sub>2</sub> F <sub>5</sub> Cl <sub>3</sub>	4.2

6	C <sub>2</sub> F <sub>5</sub> Cl <sub>4</sub>	parts
7	CFCI <sub>3</sub> CCl <sub>3</sub>	7.7
8	CClF=CCl <sub>2</sub>	12.9
9	CCl <sub>2</sub> =CCl <sub>2</sub>	0.7
		262.7

There was 100% conversion of the hydrocarbon starting material and the carbon tetrachloride together with the perhalo C<sub>2</sub> compounds were available for recycling.

#### Example 4

The reactor used was 210 cm in length. At a temperature of 600°C a gaseous mixture of propene 14.1 parts, chlorine 301 parts, hydrogen fluoride 42 parts and perchloroethylene 342 parts was passed into the reactor over a period of 3 hours giving a contact time of 10.7 seconds. The product after purification as described in Example 1 was analysed by known techniques and shown to comprise a mixture of perchlorofluorocarbons of approximate composition shown below:—

		parts
1	CF <sub>2</sub> Cl	7.8
2	CFCI <sub>3</sub>	36.7
3	CFCI <sub>2</sub>	54.8
4	CCl <sub>4</sub>	25.2
5	CCl <sub>2</sub> =CCl <sub>2</sub>	315
6	CFCI=CCl <sub>2</sub>	5.4
7	CFCI—CCl <sub>3</sub>	9.7

Approximately the same amount of perchloroethylene left the reactor as entered it. Compounds 4 to 7 were available for recycling.

#### Example 5

Using the reactor of length 105 cm, which was maintained at 631°C, a gaseous mixture of methyl acetylene 21 parts, chlorine 390 parts and hydrogen fluoride 138 parts was passed through the reactor over a period of 3 hours giving a contact time of 3.5 seconds. The product after washing and drying was shown to comprise a mixture of chlorofluoromethanes. The precise composition was:—

		parts
1	CFCI <sub>3</sub>	57.1
2	CF <sub>2</sub> Cl <sub>2</sub>	31.6
3	CF <sub>3</sub> Cl	0.2
4	CCl <sub>4</sub>	3.1
5	C <sub>2</sub> F <sub>5</sub> Cl <sub>2</sub>	0.4
6	C <sub>2</sub> F <sub>5</sub> Cl <sub>3</sub>	0.8
7	C <sub>2</sub> F <sub>5</sub> Cl <sub>4</sub>	9.1
8	C <sub>2</sub> FCl <sub>5</sub>	4.6
9	C <sub>2</sub> Cl <sub>5</sub>	1.3
10	CClF=CCl <sub>2</sub>	5.2
11	CCl <sub>2</sub> =CCl <sub>2</sub>	7.8

Compounds 4 to 11 were available for recycling.

## Example 6

The reactor of length 210 cm was used in this Example, with the reactor at 640°C, a gaseous mixture of perchloroethylene 155 parts, hydrogen fluoride 182 parts, and chlorine 315 parts was passed through the reactor over a period of 4.5 hours giving an approximate contact time of 4.6 seconds. Analysis of the organic fraction of the reactor off-gases showed it to comprise a mixture of chlorofluorocarbons, the composition being:—

		parts
15	1 CFC <sub>1</sub> <sub>3</sub>	27.0
	2 CF <sub>2</sub> Cl <sub>2</sub>	19.6
	3 CF <sub>3</sub> Cl	0.2
	4 CCl <sub>4</sub>	2.6
	5 C <sub>2</sub> Cl <sub>5</sub> F <sub>3</sub>	1.5
	6 C <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub>	1.9
20	7 C <sub>2</sub> Cl <sub>3</sub> F	4.3
	8 C <sub>2</sub> Cl <sub>4</sub>	14.1
	9 CFC <sub>1</sub> =CCl <sub>2</sub>	1.3
	10 CCl <sub>2</sub> =CCl <sub>2</sub>	58.4

## Example 7

The reactor of length 105 cm was used in this Example. A gaseous mixture of 87 parts of chlorinated hydrocarbons (approximate composition trichloroethylene 77 parts, 1,1,2-trichloroethane 11 parts, vinylidene chloride 4 parts, cis and trans 1,2-dichloroethylene 6 parts, and tetrachloroethylene 2 parts) was passed with 55 parts hydrogen fluoride and 114 parts chlorine through the reactor maintained at 600°C over a period of 2 hours. The contact time was calculated to be 6 seconds. After washing and drying the volatile products were condensed and the liquid was shown to be a mixture of CF<sub>3</sub>Cl 13 parts, CF<sub>2</sub>Cl<sub>2</sub> 41 parts, CFC<sub>1</sub><sub>3</sub> 5 parts, C<sub>2</sub>F<sub>4</sub>Cl<sub>2</sub> 9 parts and C<sub>2</sub>F<sub>5</sub>Cl<sub>2</sub> 32 parts.

## Example 8

Under conditions described in the previous Example a gaseous mixture of 108 parts of chlorinated hydrocarbons (approximate composition, chloroform 27 parts, carbon tetrachloride 27 parts, vinylidene chloride 2 parts, cis and trans 1,2-dichloroethylene 6 parts, 1,1-dichloroethane 3 parts, trichloroethylene 14 parts and ethylenedichloride 21 parts) was passed with 148 parts chlorine and 69 parts hydrogen fluoride through the reactor at 600°C. An approximate contact time of 5.9 seconds was obtained. After washing and drying the volatile products were condensed. Analysis indicated that the liquid was a mixture of chlorofluorocarbons having the approximate composition CF<sub>3</sub>Cl 17 parts, CF<sub>2</sub>Cl<sub>2</sub> 66 parts, CFC<sub>1</sub><sub>3</sub> 11 parts, C<sub>2</sub>F<sub>4</sub>Cl<sub>2</sub> 1 part, C<sub>2</sub>F<sub>5</sub>Cl<sub>2</sub> 5 parts.

## Example 9

The apparatus used was as described in Example 7. A gaseous mixture of 2,2-difluoropropane 40.5 parts (obtained from the

addition of hydrogen fluoride to methylacetylene), chlorine 336 parts and hydrogen fluoride 106.5 parts, was passed over a period of 3 hours (giving a contact time of 9.9 seconds) through the reactor maintained at 575°C. The exit gases after washing and drying were condensed and analysed. Analysis indicated that the liquid was a mixture of chlorofluorocarbons together with some chlorocarbons, the composition being:—

		parts	
	1 CFC <sub>1</sub> <sub>3</sub>	33.8	
	2 CF <sub>2</sub> Cl <sub>2</sub>	31.0	75
	3 CF <sub>3</sub> Cl	2	
	4 CCl <sub>4</sub>	19	
	5 C <sub>2</sub> Cl <sub>5</sub> F <sub>3</sub>	17	
	6 C <sub>2</sub> Cl <sub>4</sub> F	34.1	
	7 C <sub>2</sub> Cl <sub>4</sub>	4.9	80
	8 CCIF=CCl <sub>2</sub>	8.0	
	9 CCl <sub>2</sub> =CCl <sub>2</sub>	11.2	

## Example 10

The apparatus used was as described in Example 7. A gaseous mixture of 2-fluoropropane 26.5 parts (obtained by the addition of hydrogen fluoride to propene), chlorine 289 parts and hydrogen fluoride 115 parts was passed over a period of 25 hours (giving a contact time of approximately 3.6 seconds) through the reactor which was kept at 604°C. The reactor off-gases after washing and drying were analysed and shown by conventional analytical techniques to comprise essentially a mixture of chlorofluorocarbons together with some chlorocarbons the composition being:—

		parts	
	1 CFC <sub>1</sub> <sub>3</sub>	29.1	
	2 CF <sub>2</sub> Cl <sub>2</sub>	11.6	
	3 CF <sub>3</sub> Cl	1.5	100
	4 CCl <sub>4</sub>	3.1	
	5 C <sub>2</sub> F <sub>4</sub> Cl <sub>2</sub>	0.8	
	6 C <sub>2</sub> Cl <sub>5</sub>	4.2	
	7 C <sub>2</sub> Cl <sub>4</sub>	4.8	
	8 CCIF=CCl <sub>2</sub>	4.3	105
	9 CCl <sub>2</sub> =CCl <sub>2</sub>	24.9	

## WHAT WE CLAIM IS:—

1. A process for the manufacture of a perchlorofluoromethane which comprises bringing into reaction an aliphatic hydrocarbon having three carbon atoms or a halogenated aliphatic hydrocarbon (as hereinbefore defined) having one to three carbon atoms with hydrogen fluoride and chlorine in the absence of a particulate catalyst at a temperature in the range 525°C to 700°C.
2. A process as claimed in Claim 1 in which the reaction temperature is at least 550°C.
3. A process as claimed in Claim 1 or Claim 2 in which the reaction temperature is in the range 575°C to 625°C.
4. A process as claimed in any one of the preceding claims wherein the organic starting material comprises chlorinated residue ob-

5

1,359,023

5

tained in the production of chlorinated aliphatic hydrocarbons, the said residues comprising mixtures predominating in partially chlorinated C<sub>3</sub> hydrocarbons.

5. A process as claimed in any one of Claims 1 to 3 wherein the organic starting material comprises a chlorinated or fluorinated hydrocarbon containing three carbon atoms.

10. 6. A process as claimed in any one of Claims 1 to 3 wherein the organic starting material comprises an aliphatic hydrocarbon containing three carbon atoms.

15. 7. A process as claimed in any one of Claims 1 to 3 wherein there is employed a starting material predominating in a partially-chlorinated C<sub>3</sub> hydrocarbon and in which there are employed from 1.5 to 5 moles both of hydrogen fluoride and of chlorine per mole of starting material.

20. 8. A process as claimed in any one of Claims 1, 2, 3 and 6 wherein the organic starting material is a C<sub>3</sub> hydrocarbon and wherein there are employed at least 3 moles and up to 15 moles of hydrogen fluoride per mole of C<sub>3</sub> hydrocarbon.

25. 9. A process as claimed in Claim 8 wherein there are employed at least 5 moles of hydro-

gen fluoride and up to 15 moles of hydrogen fluoride per mole of C<sub>3</sub> hydrocarbon.

10. A process as claimed in Claim 8 or Claim 9 wherein there are employed from 5 moles to 12 moles of chlorine per mole of C<sub>3</sub> hydrocarbon.

11. A process as claimed in any one of the preceding claims in which chloro-, chlorofluoro-, or fluorocarbon by-products are recycled to the process.

12. A process for the manufacture of perchlorofluoromethanes substantially as described with reference to and as shown in any one of Examples 1 to 5.

13. A process for the manufacture of perchlorofluoromethanes substantially as described with reference to and as shown in any one of Examples 6 to 8.

14. A process for the manufacture of perchlorofluoromethanes substantially as described with reference to and as shown in Example 9 or Example 10.

15. A perchlorofluoromethane whenever manufactured by a process claimed in any of the preceding claims.

D. VINCENT,  
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.